ARKIV FÖR KEMI

UTGIVET AV

KUNGL. SVENSKA VETENSKAPSAKADEMIEN

Band 16 nr 38

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diss. Upps.

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A low-temperature study of some simple hydrogen-bonded structures

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ALMQVIST & WIKSELL

GÖTEBORG · STOCKHOLM · UPPSALA

1960

A low-temperature study of some simple hydrogen-bonded structures

BY

IVAR OLOVSSON

FIL. LIC., NORRL.

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IN THE LECTURE HALL OF THE INSTITUTE OF CHEMISTRY,
NOVEMBER 26, 1960, AT 10 A.M., FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.
IN ADDITION TO THIS SURVEY THE PAPERS NUMBERED 1–5
IN THE LIST OF REFERENCES WILL BE
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UPPSALA 1960
ALMQVIST & WIKSELLS BOKTRYCKERI AB

ARKIV FÖR KEMI Band 16 nr 38

Communicated 12 October 1960 by GUNNAR HÄGG and KARL MYRBÄCK

A low-temperature study of some simple hydrogen-bonded structures

By IVAR OLOVSSON

With 9 figures in the text

In many simple inorganic compounds, hydrogen bonds play a major part in determining the arrangement in the solid state, but the crystal structures are in some cases still unknown. This may be partly due to experimental difficulties, as many such substances are gases or liquids at ordinary temperatures. A study of the bonding system in such simple cases should be of particular importance for the development of a theory of the hydrogen bond. In more complicated compounds other factors affect the arrangement to a much larger extent and make a detailed interpretation more difficult. The present author thus became interested in undertaking single-crystal X-ray studies of some of the addition compounds between ammonia and the ammonium halides. The structures of $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$, $NH_4I \cdot 3NH_3$, and $NH_4I \cdot 4NH_3$ were investigated [1, 2]. During this work it became apparent that a single-crystal study of ammonia itself would be of considerable interest in confirming the structure earlier obtained by powder methods and to improve the knowledge of the atomic positions. The structures of both NH_3 and ND_3 were then studied independently [3][1]. The structure of ammonia hemihydrate, $NH_3 \cdot \frac{1}{2}H_2O$, had previously been studied and it was therefore natural to continue with an investigation of the closely related compound, ammonia monohydrate, $NH_3 \cdot H_2O$ [4]. Finally, the partial resemblence of this structure to that of ice directed the interest to a study of the structure of hydrogen peroxide dihydrate, $H_2O_2 \cdot 2H_2O$ [5].

The details of the work on each compound are described in refs. [1–5]. A summary of this work is given here and some general aspects, particularly concerning the hydrogen bonds, are presented. The low-temperature apparatus is also described in some detail below, as a complete description has not been given in the separate papers.

Experimental

The compounds studied are liquids or gases at ordinary temperatures and special techniques have to be applied when preparing samples for the X-ray studies. All samples were kept in thin-walled glass capillaries; the section exposed to the X-rays had a diameter of 0.1–0.2 mm (wall thickness 0.01–0.02 mm). In those cases where

[1] This was done during a two-year stay at Professor D. H. Templeton's laboratory at the Lawrence Radiation Laboratory of the University of California, Berkeley, U.S.A.

the composition was obtained by direct weighing of the substance in the capillary, it was essential to use a large enough sample, and the rest of the capillary (not exposed to the X-rays) then had a diameter of about 2 mm. The ammines of the ammonium halides were prepared by condensing ammonia over the salt in such capillaries. Weighing the capillary when empty, after filling with salt, and after condensing ammonia and melting off, gave the composition of the sample; the desired composition was obtained by way of trial. The samples of ammonia monohydrate were prepared in a similar way. The samples of NH_3 and ND_3 were obtained by direct condensation into cylindrical capillaries of 0.1–0.2 mm diameter. The hydrogen peroxide and water could easily be mixed to the correct composition in a conventional manner and the mixture then sucked into the capillaries.

The ammonia, water, and hydrogen peroxide used for the preparation of the samples were purified by repeated distillation; the ammonium halides (C.P.) were recrystallized from water (NH_4Cl and NH_4Br) or alcohol (NH_4I) [6].

The structure determinations were based in all cases on three-dimensional X-ray data obtained from single crystals using Weissenberg cameras modified for low-temperature work. The single crystals were then grown in the camera in a conventional manner; some details are given in the next section. The low-temperature apparatus has been continuously improved in order to obtain lower temperatures and a simplified handling. As a complete description has not been given in the separate papers, some of the details of the present set-up are described below.

The low-temperature apparatus

The present apparatus at Uppsala is a modification of a Weissenberg goniometer manufactured by Nonius, Holland. A description of the original apparatus has been published earlier [7], and only essential differences will therefore be described. The main features are illustrated in Fig. 1. The cooling gas is air taken from the compressed air line, and carefully dried through a couple of metal tubes (diameter 7 cm, total length 3 m) filled with calcium chloride and (at the exit end) other more effective drying agents. Before the air enters at *A* it is precooled by passing through a metal spiral immersed in liquid air or dry ice. The water vapour still remaining is condensed here and this tube has therefore a quite large diameter (about 3 cm) and is capable of removing a large amount of water without interrupting the air-stream. Alternatively, the dry, precooled air may be obtained by boiling directly from a liquid-air container. The air is then passed through the carefully insulated and flexible metal tube *A*. There is evidently little risk of water condensation here and this tube can therefore be chosen with a rather small diameter (about 8 mm) to make it more flexible; it is made from a bellowed phosphorbronze tube. A quite flexible insulation is obtained by wrapping sheet glass-wool around the tube and covering with plastic (use of ordinary glass-wool makes the insulation too stiff). The final cooling of the air is obtained in the metal spiral (*B*) inside the glass Dewar (*C*) filled with liquid air. With precooled air, one filling lasts 6–9 hours (the volume of the Dewar is about 3 l). The tube in *B* is of the same material as *A* but has a larger diameter (about 1.5 cm); tubes having a smaller diameter tended to block with ice. Surprisingly enough, this has also happened when the gas has been obtained by direct boiling from a liquid-nitrogen container (entry of water from the atmosphere seems to be impossible). The air finally passes through the glass Dewar tube (*D*), which ends at a

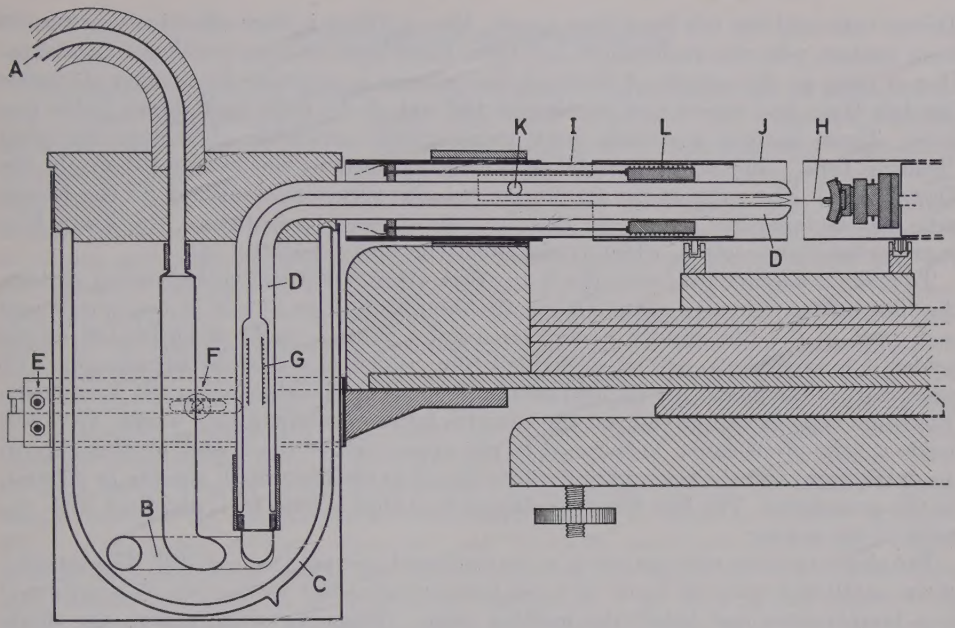


Fig. 1. Some details of the low-temperature apparatus of the Weissenberg goniometer. The different parts are described in the text.

distance of 1–2 mm from the tip of the capillary (*H*) containing the sample. By this arrangement, the air is very little heated after the final cooling in *B* and, as the well insulated tube (*D*) begins close to the bottom of the Dewar container (*C*), the temperature of the air is practically independent of the level of the cooling medium. The temperature at the tip of the capillary is constant within one or two degrees. The Dewar (*C*) is rigidly attached to the upper part of the Weissenberg goniometer but can be adjusted vertically or horizontally (after loosening the screws (*E*) or (*F*), respectively). The flexibility of the tube *A* makes it simple to turn the upper part of the goniometer when setting for the higher diffraction layers. A heating coil (*G*) inside the Dewar tube makes it possible to adjust the temperature to any desired value, for instance, when growing the crystals.

The temperature is measured with a copper–constantan thermocouple inside the Dewar tube with the cold junction 1–2 mm from the tip of the capillary. The wires run inside the tube and are there very thin (diameter about 0.1 mm) to avoid disturbing the laminar flow of the air. The thermocouple was calibrated by comparison with known melting points of samples placed at *H*. The layer-line screen is in two parts, the left of which originally also served as a support for the cooling tube. However, the setting of this tube was then very easily disturbed when the layer-line screen was shifted to higher layers. The left part was therefore separated into two pieces of which the inner (*I*) is always kept fixed and serves as a support for the cooling tube. The outer cylinder (*J*), which serves as the left layer-line screen, slides over *I* and a tongue extends to the left so that it can be fixed with a screw (*K*). The slit between the left and right layer-line screen is covered with thin mylar tape when working at low temperatures; when the slit is so covered the cooling gas passes out between the

Dewar tube and the left layer-line screen. The capillary is thus effectively protected from contact with the atmosphere and there have been no icing problems. Condensation or icing on the outside of the layer-line screens is overcome by a heater (L) inside the left layer-line screen and another at the end of the right (not shown in the picture). These heaters are made from commercially available glass-wool insulated "heating tape" (the same material is preferably used in the heater (G) inside the Dewar tube). The support for the heater (L) also serves as a support for the Dewar tube. As the layer-line screen can thus be kept at room temperature, the X-ray film is protected from cooling, which could affect the film sensitivity [8].

To make it possible to change the X-ray film without disturbing the cooling system, the film holder is in two parts. Originally the film had to be cut in two pieces and each part of the film holder loaded separately. With a slight modification of the holder it is possible to use an undivided film, which has obvious advantages. The upper part of the holder is equipped with a film clip at the edge facing the X-ray tube (the same type of clip as that on the cassette for room-temperature work). The film, inside a light-proof cover, is fastened to the upper half of the holder by this clip (in the dark-room) and the free end of the film placed in the lower half, already in position on the goniometer. The film length is adjusted so that a good fit is obtained with the walls of the holder.

The single crystals were grown in a conventional manner (see e.g. [9]). The samples in the capillaries were all liquid at room temperature. The cooling was first adjusted to a temperature just below the melting point. (When for some reason the single crystals are difficult to grow it is particularly important to adjust the temperature so that the crystal grows as slowly as possible.) Ordinarily the sample is still liquid due to super-cooling, and crystallization is therefore induced by touching with a cold object, such as a metal wire cooled in dry ice or liquid air. The polycrystalline mass obtained this way is then melted (by touching with a finger or some other means) except for a tiny piece at the end of the capillary. From this seed the crystal is allowed to grow and, if not a single crystal, almost everything is remelted and the crystal allowed to grow again, possibly this time starting at the other end from a small residual piece of the crystal just grown. This procedure is repeated until a satisfactory single crystal is obtained. Large gas bubbles generally make the growing of good crystals more difficult, although in some cases they have been an advantage in stopping the growth of all extra crystals except one, which continues beyond the bubble. With samples consisting of two components, one being much more volatile than the other, it is, of course, very important that the sample has a homogeneous composition before the crystal-growing is started. The capillaries are therefore first held at a uniform temperature for some time and the liquid then frozen quickly. If the capillary is not quite filled with liquid it is particularly important that the part of the capillary where the crystal is later grown is filled with liquid from the beginning. Distillation otherwise occurs and the crystals obtain incorrect compositions.

The growth of the crystals was followed with a polarizing microscope. The polarizer and analyzer (made from polaroid film) were coupled so that they remained crossed when turned. Although the polarizing device was certainly of great help for checking the perfection of the crystals, the final test in the X-ray photographs in many cases revealed imperfections that were difficult to detect with the existing microscope; this was particularly noticeable when the crystals grew as long twinned needles. In the case of ammonia (which is cubic) the polarizing device was of no use and each crystal grown had to be tested by X-ray photographs.

Determination of the structures

The separate crystal structures were determined from complete sets of equi-inclination Weissenberg photographs taken with Cu-K radiation. The relative intensities were estimated visually by the use of the multiple-film technique and comparison with an intensity scale. The usual corrections for the Lorentz, polarization and velocity factors were applied. The atomic positions were determined from three-dimensional Patterson and electron density maps and subsequently refined by difference syntheses and least-squares methods. For these calculations the IBM 650 and 701 computers at Berkeley have been used almost exclusively. The original least-squares program LSII [10], was then modified for each particular space group. In this program, no off-diagonal terms are used except those between the x and z coordinates of the same atom. The program minimizes the quantity $R_3=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; the system of choosing the weighting factor w in this expression is described in the separate papers [1–5]. The atomic coordinates (except for hydrogen), individual isotropic temperature factors (B in the expression exp $(-B\sin^2\theta/\lambda^2)$), and an overall scale factor were the parameters refined. The scaling between the separate layers was determined by comparison of common reflexions, or from the relative exposure times of the layers. In some cases, the scale factor for each layer was actually refined individually in the last cycles, but the deviation of the final scale factors from their mean value was quite small. Because of neglection of the off-diagonal terms in the least-squares program, the convergence was sometimes rather slow. The refinement process therefore had to be carefully watched and great care taken to make certain that the refinement had converged to the best minimum; this is also most important if the calculated standard deviations are to have any real meaning (see further below). The refinement was in general discontinued when the shifts of the coordinates in the last cycles were less than about one-tenth of the standard deviation for the coordinate in question.

The process of least-squares refinement was repeatedly checked by comparison with F_o-F_c maps calculated at different stages. No significant extra features or deviations from the atomic positions suggested by the least-squares refinement, were indicated in these maps. The extra peaks in the difference maps (based on all atoms except hydrogen) could thus be rather conclusively attributed to the hydrogen atoms. These peaks all appeared close to the places expected for hydrogen from chemical considerations. In the cases where the hydrogen peaks were significantly removed from the lines connecting the heavy atoms the experimental positions always corresponded to more normal bond angles within the molecules. The hydrogen atoms were in some cases included in the least-squares calculations (with fixed parameters) but their influence on the results was very small.

The standard deviations of the atomic coordinates were obtained from the ordinary least-squares expression with a diagonal approximation. It should be pointed out that these standard deviations have no real meaning unless the refinement has converged to the best minimum. The least-squares method gives the accuracy of the best fit, but no direct information about possible systematic deviations of the parameters from these best values (cf. [11]). Actually, the diagonal approximation does not give the true standard deviations of the best fit, but the error is estimated to be almost negligible in the present cases. Reasonably symmetric three-dimensional data have been generally used and the errors in Å are then as expected, approximately isotropic (cf. [12]). In principle, crystallographic independence does not necessarily

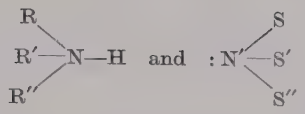
imply statistical independence of coordinates [12] and, for correct evaluation of the standard deviations of bond distances and angles, all correlation coefficients should therefore be known. However, no information about the correlation is obtained when using the diagonal approximation, but the error involved on neglecting this kind of correlation is estimated to be of little importance here. The influence on the standard deviations of errors in the unit cell parameters were in all cases found to be of negligible magnitude.

Discussion of the hydrogen bonds

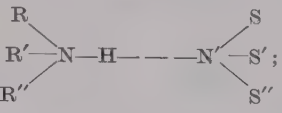
The separate structures were described in detail in the earlier papers [1–5]. In the present section, the hydrogen bonds are discussed and compared with those in some related compounds. Only the structural features of immediate interest for the present discussion are summarized below and the individual papers should be consulted for further information.

The hydrogen bond is known to be mainly electrostatic in character and is formed only between highly electronegative atoms such as fluorine, oxygen, chlorine and nitrogen. As a simple model for the hydrogen bond, X–H—Y, between two atoms X and Y, we may use the following picture: when hydrogen is bonded to the strongly electronegative element X, the bond electrons are more attracted to atom X leaving an effective positive charge on the hydrogen atom causing attraction for the second electronegative atom Y. Many properties may be given quite satisfactory explanation in terms of a simple electrostatic model for the hydrogen bond, but there are details that cannot be readily accounted for in this way and many different theories have thus been developed. A general discussion of the hydrogen bond is given in a book by Pimentel & McClellan [13]; other important sources of information are refs. [14, 15] and many excellent review articles (for references see [15], p. 449). Considerable theoretical development is still needed before all of the characteristics of hydrogen bonding can be satisfactorily explained.

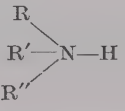
For the following discussion on the variation of the hydrogen-bond lengths, it seems profitable to make use of four distinct concepts: (*A*) electrostatic interaction, (*B*) delocalization effects, (*C*) repulsive forces, (*D*) dispersion forces. The term "electrostatic interaction" (*A*) denotes here only such coulombic forces that would arise if the interacting species were brought together without any deformation of the charge clouds or any electron exchange. This is of course quite impossible practically and the resulting permanent distortion of these clouds is represented by the delocalization term (*B*). The London dispersion forces (*D*) arise from the coupling of the motion of the electrons in the separate atoms. Finally, some repulsive forces (*C*) must exist, and they arise as a result of the Pauli Exclusion Principle when the saturated electron clouds of the different atoms overlap. These different effects are further discussed by Coulson in his review of the hydrogen bond (ref. [14], p. 339). (The names of the separate effects (*A*)–(*D*) are of course in a sense artificial, as all interactions which we consider here are essentially electrostatic. It is also well known that the forces acting on each nucleus in a molecule may be calculated simply by the principles of classical electrostatic theory from the charges and positions of the other nuclei and electrons, without any reference to exchange or resonance forces at all [16, 17].) An attempt is made in the following to relate some systematic variations in the hydrogen bond lengths to differences in the electrostatic interaction. Consider, for instance, the two molecules



interacting with each other to form a hydrogen bond:



R and S may here be lone-pair electrons, hydrogen atoms or some other atoms. For a detailed discussion of the bond it would obviously be necessary to know the actual electron distribution, but this cannot be calculated with any accuracy. An estimation of the charges might be obtained from a consideration of the electronegativities of the different atoms [15]. However, the effective electronegativity is dependent on the net charge on the atom; a positive net charge results in a greater power to attract the electrons and therefore in an increased effective electronegativity, a negative net charge results in a decreased effective electronegativity. In a molecule where one atom is bonded to more than one other atom, the polarity of each of these bonds places a net charge on the atom and this charge then affects the electronegativity. It is thus obviously not possible to obtain the net charges directly from the original atomic electronegativities (see further Lindqvist [18]). In the molecule under discussion,



the charge for instance on the hydrogen atom can therefore not be accurately estimated. However, the *change* in the effective charge on hydrogen when R, R′ or R″ are substituted by others can be estimated if there is a reasonably large difference in electronegativity between the original and substituent groups. In the present compounds it seems quite safe to assume that hydrogen has a positive net charge. When R is replaced by another group with a stronger attraction for the electrons, the result is obviously an increased effective electronegativity of nitrogen and hence an increased power of this atom to attract the electrons in the N–H bond, i.e. the effective charge on the hydrogen will be increased. This increased positive charge will lead to a stronger interaction between hydrogen and the nitrogen atom of the other molecule (N′) and the distance H—N′ should decrease. However, from this it does not follow that the total distance N—N′ will also decrease, as the distance N–H may change as a result of the interaction with N′. (The N–H distance may also change slightly as a direct inductive effect of a replacement of R by some other group (cf. below).) The total effect is therefore difficult to predict with certainty. Experimentally it has been found in O–H—O bonds that the change in the O–H distance is small compared to the change in the total distance O—O. This is particularly true when the hydrogen bond is weak and the O–H distance is then also not appreciably different from that in the free molecule (cf. [13], p. 259). Less complete information for other bonds indicates the same things. It is therefore assumed that this is true also in the cases discussed below where all the hydrogen bonds are relatively weak. In the N–H—N′ bond under

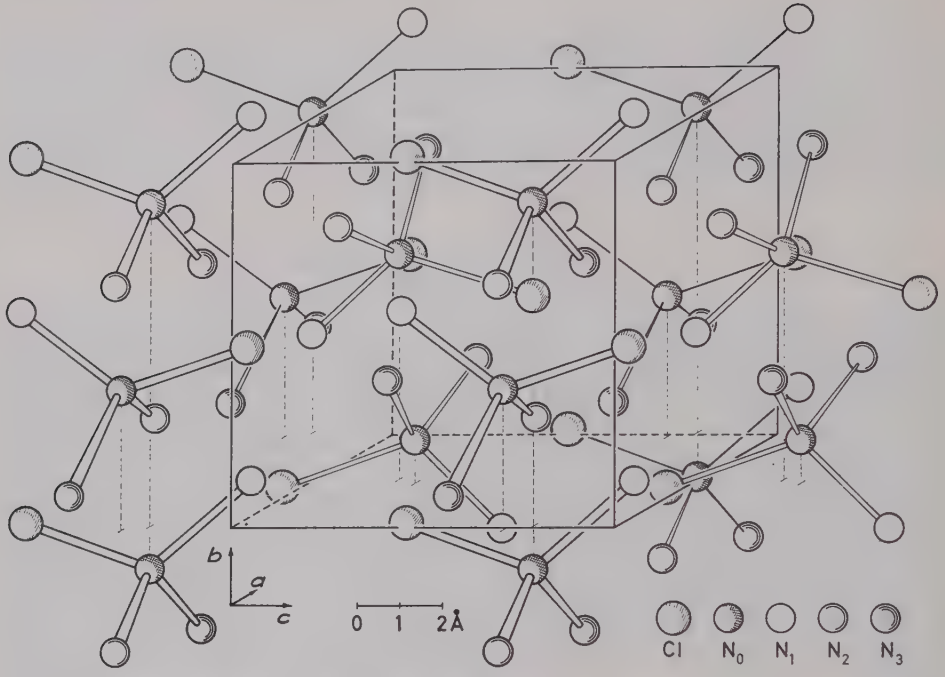


Fig. 2. The crystal structure of $NH_4Cl \cdot 3NH_3$ ($NH_4Br \cdot 3NH_3$ is isostructural; N_2 and N_3 are interchanged in certain cases in $NH_4I \cdot 3NH_3$). N_0 is nitrogen in the ammonium ion; N_1, N_2 and N_3 belong to the three ammonia molecules. The hydrogen bonds within the discrete chlorotriammineammonium tetrahedra are drawn as solid lines (cf. [1]).

discussion we would then expect a decrease in the N—N′ distance as the positive charge on hydrogen increases. The increased effective charge on N on substitution of R will naturally also contribute to this effect as it reduces the electron repulsion between the nitrogen atoms N and N′ connected by the hydrogen bond. The effect on the hydrogen-bond lengths expected on substitution of the groups attached to nitrogen (N), are completely analogous to similar inductive effects in normal chemical bonds, as discussed by Lindqvist [18]. The interaction between the two molecules would also become stronger with increased power of N′ to attract the bridge hydrogen, for instance if the lone pair of N′ were "pushed away" from N′ in the direction of the bridge hydrogen. The arguments presented may be analogously applied to other types of hydrogen bonds and should also be valid for bonds of the type N–H—Cl. In the case of a weak interaction like the hydrogen bond, it is of course most important to consider other effects that may be of comparable magnitude, for instance interaction with next-neighbor atoms. However, the qualitative agreement between the estimated and observed variations of the bond lengths in the cases discussed below seems to give some justification for the present approach.

1. *N–H—X* (*X*=*Cl,Br,I*). In $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$ and $NH_4I \cdot 3NH_3$ the three ammonia molecules and the halide ion are bonded to ammonium in a tetrahedral halidotriammineammonium group, while the forces between the different groups are apparently rather weak (Fig. 2). The hydrogen atoms of ammonium are

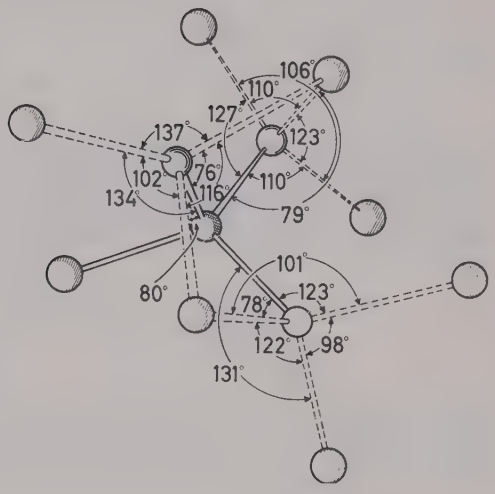


Fig. 3. The distribution of the chlorine neighbors to the ammonia molecules in $NH_4Cl \cdot 3NH_3$. Atoms are designated as in Fig. 2.

evidently involved in the bonds within this $[NH_4X(NH_3)_3]$ group. In principle, the bond between nitrogen and halogen is quite comparable with that in many other compounds like $RNH_2 \cdot HCl$ and $RNH_2 \cdot HBr$. The bonding must also be very similar to that between ammonium and halogen in the closely related compounds NH_4Cl, NH_4Br, and NH_4I. Also, in these latter cases, the hydrogen atoms are located close to the lines joining the nitrogen and halogen atoms. The distances N—X are quite comparable when the different coordination numbers are taken into consideration ([15], p. 522); in $NH_4X \cdot 3NH_3$ we may set the coordination number for ammonium equal to four, while it is six and eight in the ammonium halides with respectively sodium chloride- and caesium chloride-type structures. The N—Cl distances are 3.22 Å ($NH_4Cl \cdot 3NH_3$), 3.26 Å (NH_4Cl at 250°C, *NaCl-type*) and 3.35 Å (NH_4Cl, *CsCl-type*). The N—Br distances are 3.39 Å ($NH_4Br \cdot 3NH_3$), 3.45 Å (NH_4Br at 250°C, *NaCl-type*) and 3.50 Å (NH_4Br, *CsCl-type*). The N—I distances are 3.64 Å ($NH_4I \cdot 3NH_3$), 3.62 Å (NH_4I, *NaCl-type*) and 3.79 Å (NH_4I at −17°C, *CsCl-type*). Note, however, that all four hydrogen atoms in ammonium cannot simultaneously be located on the N—Cl line in the high temperature form of the ammonium halides (*NaCl-type*) with an octahedral coordination of the halogens around nitrogen. Here the conclusions from different experiments are that only one of the N–H bonds is directed towards halogen with relatively free rotation around the N–H—X bond axis [19–21]. A detailed comparison of the bond distances is therefore somewhat difficult.

Before continuing the comparison between N–H—X distances, it is of interest to first discuss the bonding situation for the ammonia molecules. The lone pairs of the ammonia molecules are evidently involved in the hydrogen bonds to the central ammonium ion within the $[NH_4X(NH_3)_3]$ group. Bonding between the different ammonia molecules then appears improbable. Three halide ions are located quite favorably around ammonia, such that nitrogen and the three halogen atoms form a flat pyramid (Fig. 3). However, the interaction with halogen is evidently rather weak; the average distances are: N—Cl = 3.59 Å, N—Br = 3.72 Å, N—I = 3.86 Å. The ammonia molecule probably directs its threefold axis along the hydrogen bond

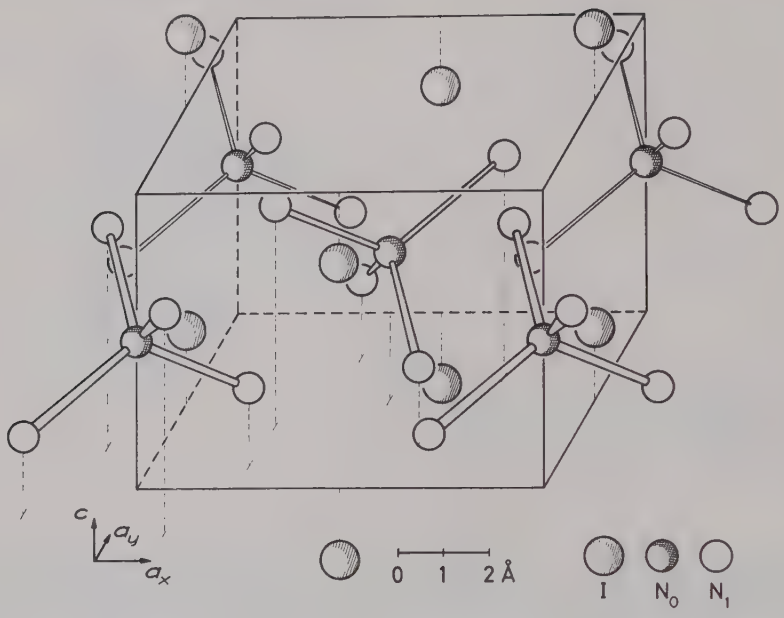
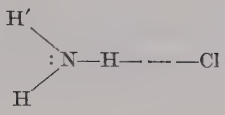


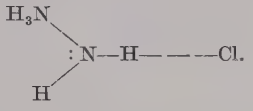
Fig. 4. The crystal structure of $NH_4I \cdot 4NH_3$. N_0 is nitrogen in ammonium, N_1 belongs to ammonia. The hydrogen bonds within the discrete tetrammineammonium tetrahedra are indicated (cf. [2]).

to ammonium, but may then be turned in such a way that its hydrogen atoms approach the lines connecting nitrogen and halogen (the evidence from the difference maps points definitely in this direction). With this interpretation of the structure we may possibly again speak about some kind of N–H—X bonding, but evidently much weaker than in the cases discussed previously. The preceding discussion of the bonding situation of ammonia applies also to $NH_4I \cdot 4NH_3$. Here, the four ammonia molecules are hydrogen-bonded to ammonium as tetrahedral tetrammineammonium groups with rather weak forces between the different groups (Fig. 4). The distribution of neighbors around ammonia is very similar to that in the triammines; the three N—I distances are 3.96, 4.15 and 4.16 Å.

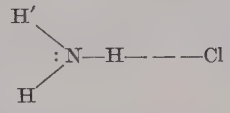
When we now compare the bonding between ammonium and halogen in $NH_4X \cdot 3NH_3$ and NH_4X on one hand, with that between ammonia and halogen on the other, it is apparent that there are great formal similarities. If, in accordance with the discussion above, we consider the three halide ions and ammonium as the bonding neighbors to ammonia, the number of groups coordinated around ammonia is evidently comparable with that around ammonium. The shorter distance between ammonium and halogen could be said to be simply due to the positive charge of ammonium. (In calculations of the lattice energies of NH_4X, the ammonium ion has generally been considered to be a uniformly charged sphere, cf. [15], p. 463 and [22].) However, in order to compare the different bonds now discussed, a more detailed consideration of the interaction is necessary. Application of the concepts introduced in the beginning of this section appears to be convenient for this purpose. Let us commence with a presumed hydrogen bond between ammonia and a chloride ion:



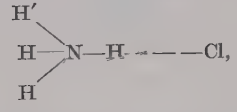
(in $NH_4Cl \cdot 3NH_3$ equal to 3.59 Å). Replacing H′ with the more electronegative groups NH_2 or NH_3 would lead to an increased electrostatic interaction according to the earlier discussion. An example of the latter replacement is hydrazinium monochloride, N_2H_5Cl, where there seems to exist two such hydrogen bonds, conveniently written as



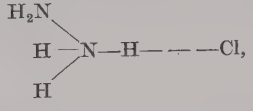
The bond lengths are 3.43 and 3.49 Å (there is also a distance N—Cl equal to 3.26 Å but the hydrogen atoms are, from geometrical considerations, apparently not directly involved in this bond [23]). Addition of an atom like hydrogen to the lone pair of ammonia in



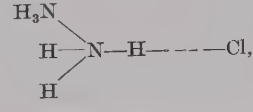
should lead to an even stronger electrostatic effect, as this addition would considerably increase the effective charge on the bridge hydrogen (and also decrease the electron repulsion between nitrogen and chlorine). The length of the hydrogen bond in this case,



is accordingly equal to 3.22 Å in $NH_4Cl \cdot 3NH_3$ (and also about the same in NH_4Cl, if the coordination number is reduced to four, as discussed earlier). Replacing H′ in the last bond with a NH_2 or NH_3 group would increase the electrostatic effect still more. In hydrazinium monochloride, N_2H_5Cl, there seems to exist two such hydrogen bonds,



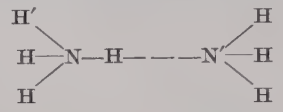
of 3.12 Å (a third distance equal to 3.41 Å is apparently not involving hydrogen, cf. above). In hydrazinium dichloride, $N_2H_6Cl_2$, all the bonds,



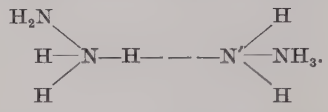
are equal to 3.10 Å [24].

An analogous comparison is more difficult for the N–H—Br and N–H—I bonds as the experimental data are here less complete and accurate, but the trends in the bond lengths appear to be the same.

2. *N–H—N*. The mean value of the three N–H—N distances within the $[NH_4X(NH_3)_3]$ group is 2.94 Å in $NH_4Cl \cdot 3NH_3$ (Fig. 2). 2.90 Å in $NH_4Br \cdot 3NH_3$, and 2.90 Å in $NH_4I \cdot 3NH_3$. The same distance within the $[NH_4(NH_3)_4]$ group in $NH_4I \cdot 4NH_3$ (Fig. 4) is 2.96 Å. When applying the earlier arguments, one would expect an increased electrostatic interaction if H′ in the bond

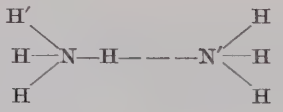


was replaced by NH_2 group. However, no compound seems to have been studied in which a hydrazinium ion is bonded to ammonia. In hydrazinium monochloride, N_2H_5Cl, one of the bonds may be formulated as

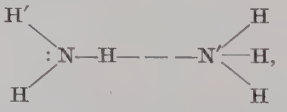


The substitution of a hydrogen in ammonium by NH_2, giving the left molecule, would tend to shorten the hydrogen bond as just mentioned. The bond, however, is no longer to an ammonia molecule on the right side. The right molecule may be considered as ammonia in which one hydrogen has been replaced by a NH_3 group. It is clear that this substitution will decrease the negative charge on N′ considerably, leading to a lengthening of the hydrogen bond. It is therefore somewhat difficult to predict the total effect on the bond length. The experimental value is 2.95 Å [23].

If one of the hydrogen atoms in



were taken away, leaving a lone pair:



a strong decrease in the electrostatic effect would be the result. The corresponding bond is found in solid ammonia (Fig. 5), but is even longer than expected, 3.38 Å. However, this may be partly due to the fact that the lone pair of N′ is apparently used for three such hydrogen bonds, and may therefore be less favorably directed for attracting a particular hydrogen atom. In this connection the hydrogen bond length found in methylamine, CH_3NH_2 (3.18 and 3.27 Å [25]) may serve as a comparison for a bond of this type; however, some allowance must then be made for the (probably small) effect of replacing one of the hydrogen atoms by a CH_3 group. (The

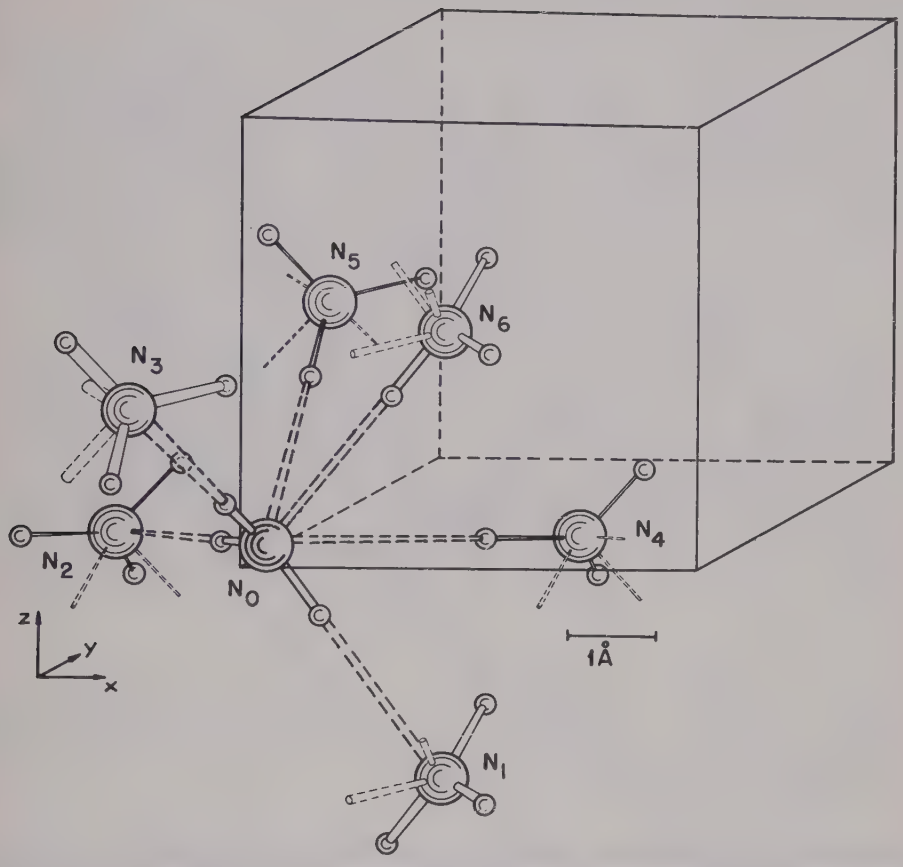
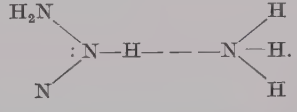
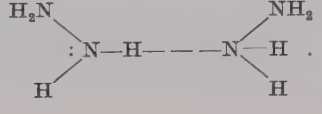


Fig. 5. The crystal structure of cubic ammonia. The six closest neighbors to N_0 are all equidistant. The hydrogen atoms are for simplicity placed on the lines connecting the nitrogen atoms, although there is experimental evidence that they are somewhat off these lines (see [3]).

hydrogen bonds may be somewhat abnormal here, too, as there are two hydrogen atoms but only one lone pair on nitrogen.) A shortening of the hydrogen bond length is expected when hydrogen (H′) is replaced by a NH_2 group:



This type of bond apparently has not been studied. If in this bond we replace a hydrogen in the right ammonia molecule by NH_2, we get the bond occurring in hydrazine:



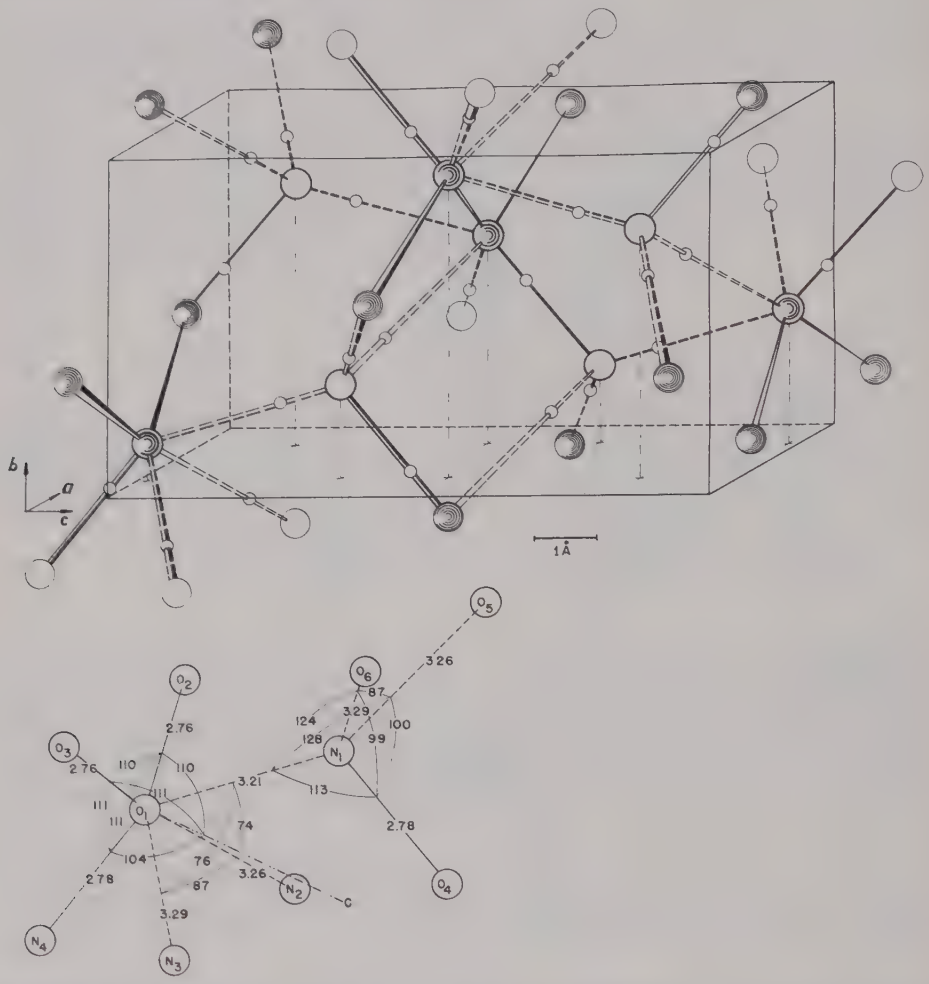


Fig. 6. The crystal structure of ammonia monohydrate. Shaded circles are oxygen; open circles are nitrogen. The short hydrogen bonds (2.76, 2.78 Å) are shown as solid lines, the long bonds (3.21, 3.26, 3.29 Å) are dotted. The centroid of these long bonds (*C*) is shown in the subfigure. The location of one of the hydrogen atoms in the water molecule is uncertain and not indicated (cf. [4]).

This last substitution would counteract the effect of the earlier substitution in the left molecule. The situation is completely analogous to that in N_2H_5Cl, discussed above, and the net effect is also similar as the experimental distances in hydrazine are 3.19, 3.25 and 3.30 Å [26]. (The situation may be complicated by the fact that there are two hydrogen atoms but only one lone pair on each nitrogen.) An average value of the bond lengths in some different types of N–H—N bonds is given as 3.10 Å by Pimentel & McClellan (ref. [13], p. 289), but such a mean value is obviously of little value for the present discussion as the character of the groups attached to the nitrogen atoms must be taken into consideration.

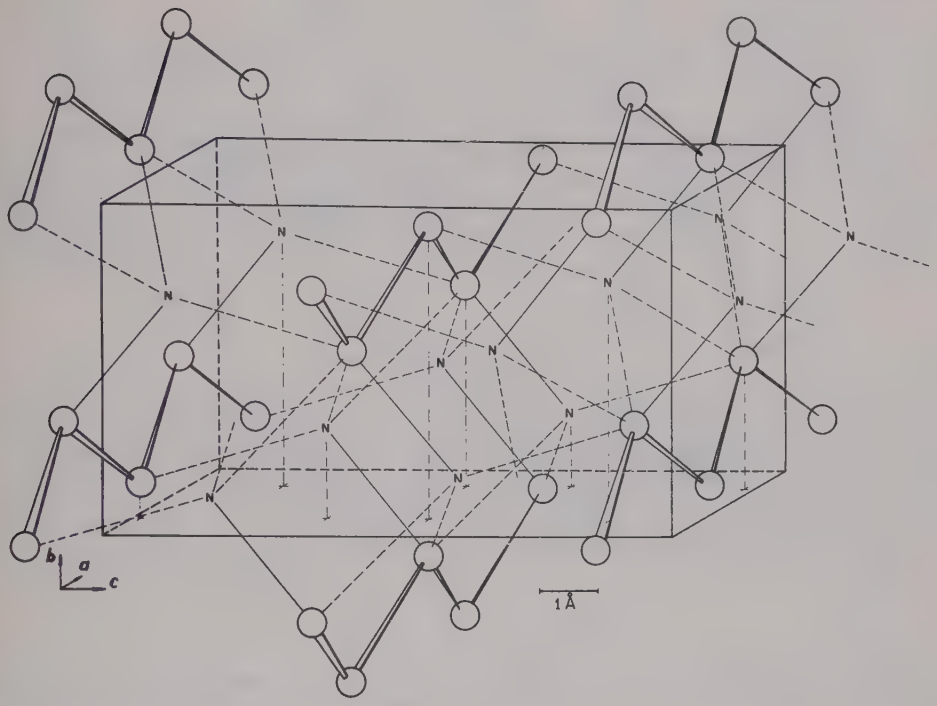


Fig. 7. The chains of water molecules in $NH_3 \cdot H_2O$ and the linkage by the ammonia molecules (cf. Fig. 6).

3. *N–H—O*. The structure of ammonia monohydrate, $NH_3 \cdot H_2O$ (Fig. 6 and 7), contains planar chains of water molecules connected by hydrogen bonds of the type O–H—O (2.76 Å). These chains are crosslinked by the ammonia molecules into a three-dimensional network by short bonds of the type O–H—N (2.78 Å) and long bonds of the type N–H—O (3.21, 3.26 and 3.29 Å). The first two types of bond are discussed below. The remarkable feature of the N–H—O bonds in this compound is that one lone pair on the oxygen atom is apparently involved in three such long bonds. The centroid of these long bonds forms, together with the three close neighbors of oxygen, an almost regular tetrahedron (Fig. 6). This is closely analogous to the situation in solid ammonia (Fig. 5) except that the oxygen atom replaces the nitrogen atom in ammonia in providing the electron pair. The shortening of the bond from 3.38 Å in ammonia (N–H—N) to the (average) value 3.25 Å in ammonia monohydrate (N–H—O), may be attributed to the stronger attraction for the bridge hydrogen by oxygen in the latter case. It is also interesting to compare with the situation in ammonia hemihydrate, $NH_3 \cdot \frac{1}{2}H_2O$, where the oxygen atom contributes roughly 2/3 of an electron pair to each bond N–H—O of average length 3.19 Å [27].

For a number of different amine compounds, the average N–H—O distance is 3.04 Å (ref. [13], p. 289), but this value is not directly comparable with the present distances as pointed out earlier. The increased electrostatic interaction when a hydrogen atom is attached to the free electron pair in

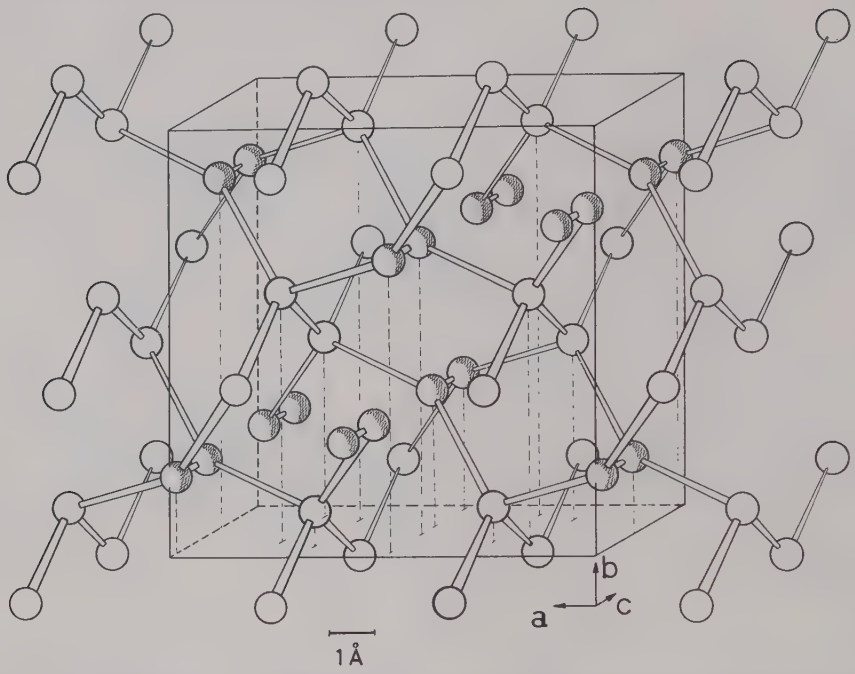
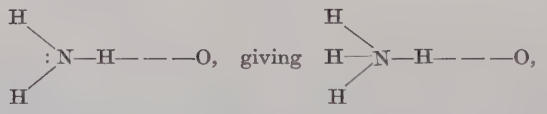


Fig. 8. The crystal structure of hydrogen peroxide dihydrate. The peroxide groups are shaded. The probable assignment of the hydrogen atoms to the bonds is indicated in Fig. 9 (cf. [5]).



is expected to shorten the distance; the average value for some ammonium compounds is 2.88 Å (ref. [13], p. 289; but with the same reservation as above).

4. *O–H—N*. There is no bonding between the ammonia molecules themselves in either $NH_3 \cdot H_2O$ (Fig. 6 and 7) or $NH_3 \cdot \frac{1}{2}H_2O$ [27], and the lone pair of nitrogen is used to form the short bond to oxygen (2.78 and 2.84 Å, respectively); a mean value of 2.80 Å has been obtained from the bond lengths in some different compounds (ref. [13], p. 289).

5. *O–H—O*. The structures of ammonia monohydrate (Fig. 7) and hydrogen peroxide dihydrate, $H_2O_2 \cdot 2H_2O$ (Fig. 8), are similar in that both contain planar zig-zag chains of hydrogen-bonded water molecules linked together by the ammonia and hydrogen peroxide molecules, respectively. The hydrogen peroxide molecules are not bonded to each other in $H_2O_2 \cdot 2H_2O$ (as pointed out earlier for the ammonia molecules in $NH_3 \cdot H_2O$). There are two more lone-pair electrons than hydrogen atoms per formula unit ($H_2O_2 \cdot 2H_2O$). The structure indicates that the number of hydrogen bonds around water is normal (four). However, each oxygen in H_2O_2 has two lone-pair electrons and one hydrogen atom but forms only two hydrogen bonds. This may

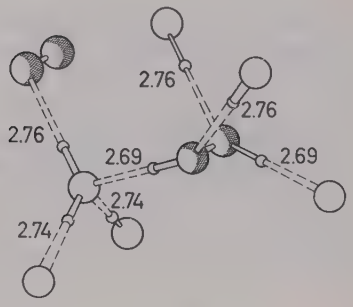
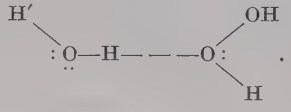
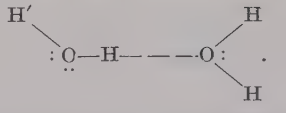


Fig. 9. The probable assignment of the hydrogen atoms to the bonds in $H_2O_2 \cdot 2H_2O$. The hydrogen atoms are for simplicity placed on the lines between the oxygen atoms, although there is experimental evidence that they are somewhat off these lines (see [5]). The orientation of the molecules is the same as in Fig. 8.

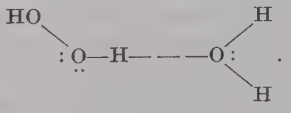
possibly effect the length of the hydrogen bond in which the lone pairs of H_2O_2 are involved (see further below). The O–H—O distances within the zig-zag chains, 2.76 Å in $NH_3 \cdot H_2O$ and 2.74 Å in $H_2O_2 \cdot 2H_2O$, are not appreciably different from those in ice, 2.76 Å [28]. The hydrogen bonds linking the hydrogen peroxide molecules to the water chains seem to be significantly different from each other, 2.69 and 2.76 Å. With the indicated positions of the hydrogen atoms (Fig. 9), the bond of 2.76 Å may be formulated as



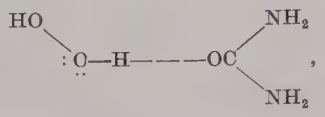
Compare this with the bond in ice,



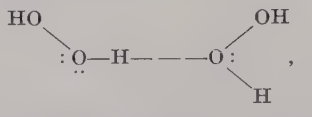
The substitution of H in the right molecule in the ice bond by OH gives the bond under consideration and should lead to decreased electrostatic interaction. It is therefore surprising that both these bonds are equally long, 2.76 Å. It was mentioned above that two lone-pair electrons are actually available in $H_2O_2 \cdot 2H_2O$ for this hydrogen bond and that may be a reason for the shortness of the present bond in the dihydrate. Let us now consider the other bond of 2.69 Å. According to the indicated hydrogen positions, this should be formulated as



This bond is derived from that in ice by replacing H′ with OH, and the expected increased interaction in the hydrogen bond may be the reason for its shortening from 2.76 Å in ice to 2.69 Å in $H_2O_2 \cdot 2H_2O$. If the right molecule (water) in the bond discussed is replaced by urea, giving



we would expect a furter decrease in the distance, as the oxygen atom in urea has a more negative charge than in water. The experimental distance is 2.63 Å in the 1:1 addition compound between urea and hydrogen peroxide [29]. The two counteracting effects when a hydrogen atom is replaced by OH in both the left and right water molecules of the ice bond, giving



may be studied in solid hydrogen peroxide. The experimental distance is 2.78 Å [30] which is about the same as that in ice. This agrees well with the net effect observed when similar simultaneous substitutions were undertaken in the N–H—N bonds discussed above. (Notice, however, that each oxygen in H_2O_2 has two lone pairs but only one hydrogen atom; cf. $H_2O_2 \cdot 2H_2O$ above.)

The discussion of the bond length variations may be extended to many other cases, but the main purpose was to treat the bonds in the present compounds. The limitations of the approach have already been mentioned and must be carefully kept in mind, especially when more complicated substances are discussed.

The isotope effect in ammonia

As a part of the investigation of solid ammonia, the unit cell dimensions of NH_3 and ND_3 were measured at two different temperatures. From the values at −196°C, $a = 5.084$ Å for NH_3 and $a = 5.073$ Å for ND_3, one notices a contraction in the unit cell of 0.011 Å when hydrogen is replaced by deuterium. In most other cases where the isotope effect has been measured, an expansion has been observed; a small contraction has been occasionally reported but little quantitative information seems to be available (cf. ref. [13], p. 293 and ref. [14], p. 45). Several theories have been advanced to explain the isotope effect. Nordman & Lipscomb [31] have given a thermal explanation, while Robertson & Ubbelodhe [32] interpreted it as a zero point energy phenomenon. On the basis of published data for O–H—O bonds, Gallagher (ref. [14], p. 45) has plotted the isotope effect as a function of the O—O distance. From this plot it seems reasonable to expect that the observed expansion for short bonds will change into a contraction for long bonds. (Gallagher has therefore suggested that the effect is the sum of two terms, one contraction and one expansion term, where the expansion term probably initially increases with decreasing O—O distance.) A contraction in the very long hydrogen bond in solid ammonia when hydrogen is replaced by deuterium, is evidently to be expected if the isotope effect behaves similarly for N–H—N and O–H—O bonds. The contraction in ammonia may be the result of two different effects. The lower zero point energy of deuterium together with the anharmonicity in the potential energy curve of the N–H group would lead to a decrease in the N–H distance. As a result, the N–H—N distance may also decrease. On the other hand,

direct measurements have shown that the dipole moment of ammonia is greater for the deuterium compound [33]. This will naturally lead to an increased interaction between the molecules and a shorter N--N distance. Nuclear quadrupole resonance measurements by O'Konski & Flautt [34] also indicate stronger bonds in the deuterium compound, as the decrease of the coupling constant upon condensation of ammonia gas (at 77°K) is larger for ND_3 (12.6 % for NH_3 and 21 % for ND_3).

General remarks

The present work has involved determination of the different crystal structures using X-ray methods. It is obvious that confirmation of the indicated hydrogen positions by neutron diffraction would be of great interest. Other physical methods have been applied in some cases and have given very valuable information about features more or less directly correlated with the structures. A large number of different investigations have thus been made on solid ammonia but rather little information has appeared so far concerning the ammines of the ammonium halides. A question of common interest in the present compounds is the extent of rotation of the ammonia molecules. In $NH_4X \cdot 3NH_3$ and $NH_4I \cdot 4NH_3$, the interaction of ammonia with neighbors is evidently quite weak and restricted rotation around the threefold axis may therefore be expected. Relatively unrestricted rotation in the present structures would probably result in transformation to some other phase at lower temperatures; this may not happen if the rotation is more restricted. Measurements of the heat capacity would be of great interest here. In solid ammonia monohydrate and ammonia, the bonds in which the hydrogen atoms of the ammonia molecules are involved are also quite weak and the possibility of restricted rotation must again be considered. Here, heat capacity measurements give no indication of phase transformations [35, 36], and the entropies approach zero at low temperatures indicating that all hydrogen bonds and structural details must be essentially ordered at the absolute zero of temperature. However, a gradually more and more restricted rotation as the temperature is lowered might still be feasible. Thus, the presence of certain absorption lines in the nuclear magnetic resonance spectrum of solid ammonia (at 90°K) has been interpreted as due to restricted rotation of the molecule about the threefold axis [37].

It was mentioned earlier that the structures of ammonia monohydrate and ammonia presented very interesting aspects of hydrogen bonds, namely that one free electron-pair apparently may be involved in more than one hydrogen bond. Few structures earlier studied have been clearly shown to contain similar kinds of hydrogen bonds; one example is ammonia hemihydrate, as mentioned earlier [27]. However, it seems probable that more such cases could be found if this possibility were kept in mind, for instance, when there are more hydrogen atoms than free electron pairs in the molecules interacting. It was pointed out earlier that in the structure of $H_2O_2 \cdot 2H_2O$ we have the opposite phenomenon, namely that there are two lone-pair electrons available for only one hydrogen bond. However, it is naturally difficult to state that both of these pairs actually take part in the hydrogen bond.

In the structure of hydrogen peroxide dihydrate, the dihedral angle of the hydrogen peroxide molecule, defined by the peroxide link and the hydrogen atoms, was found to be very approximately 130°, which is much different from that in pure hydrogen

peroxide (close to 90° [38]). This strain in the molecule may be a reason for the apparent instability of the crystal which is shown by the low melting-point of the dihydrate (−51°C) as compared to that of pure hydrogen peroxide and ice (−0.5° and 0°C, respectively). Several attempts have been made in the past to estimate the energy involved in a change of the dihedral angle. Apart from the classical paper by Penney and Sutherland [39], the survey article by Luft [40] should be consulted for further references. Spectroscopic evidence indicates that the force for twisting about the O–O bond is rather small (cf. [41]). A similar distortion may exist in the hydrazine molecule in the crystals of hydrazine monohydrate, $N_2H_4 \cdot H_2O$, as the low melting point of this substance (−52°C) compared to that of pure hydrazine and ice (+2°C and 0°C, respectively) indicates an analogous relative instability of the structure.

In the solids of the compounds $NH_4X \cdot 3NH_3$, the existence of rather isolated groups of "halidotriammineammonium molecules" $[NH_4X(NH_3)_3]$, has been demonstrated (Fig. 2). It seems rather remarkable that the addition of ammonia to the ionic compounds, NH_4X, results in the present "molecular compounds". In this respect they are some of the simplest examples of such inorganic molecular addition compounds. The "molecular" properties are quite apparent when the melting points of NH_4Cl, NH_4Br, and NH_4I (+520°, 542° and 551°C, respectively) are compared with those of $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$, and $NH_4I \cdot 3NH_3$ (about +10°, +9° and −9°C, resp.).

SUMMARY

A review is given of the earlier published structure determinations of the compounds, $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$, $NH_4I \cdot 3NH_3$, $NH_4I \cdot 4NH_3$, NH_3, ND_3, $NH_3 \cdot H_2O$ and $H_2O_2 \cdot 2H_2O$. Some general aspects are then presented, in particular concerning the hydrogen bonds. The variation of the hydrogen bond lengths in the present compounds is discussed on the basis of a simple electrostatic model for the hydrogen bond.

The special technique developed for the low-temperature X-ray study of these compounds is summarized and the apparatus is described in some detail.

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to the head of this Institute, Professor G. Hägg, for his great personal interest in this work. He introduced me to the field of low-temperature crystallography and has put every facility at my disposal. The work at Uppsala has been financially supported by grants from the Swedish Natural Science Research Council which are here gratefully acknowledged.

Part of this work was carried out during my stay at the Lawrence Radiation Laboratory of the University of California, Berkeley, U.S.A., with support of the U.S. Atomic Energy Commission. The refinements of all the structures were performed at Berkeley on the IBM 650 and 701 computers, and I am much indebted to Professor D. H. Templeton for the use of these and other laboratory facilities. I am also most grateful to him for many stimulating discussions and suggestions.

Sincere thanks are due to Mr. R. Liminga for his skilful assistance during the construction of the

low-temperature apparatus at Uppsala. I am also indebted to him and Mr. G. Larsson for their valuable help during the preliminary work on some of these compounds. Mr. S. Wahlgren has taken good care of the X-ray equipment and the conscientious secretarial work by Mrs. M. Englund and Mrs. B. Flemström has been much appreciated as well as linguistic suggestions by Dr. W. Brown.

I should like to thank Mrs. H. Ruben for a great deal of help in the laboratory at Berkeley and Drs. A. Zalkin, M. E. Senko, R. E. Jones, R. P. Dodge and Q. C. Johnson for the use of their computer codes.

Finally, I wish to thank Dr. I. Lindqvist and my colleagues at Uppsala and Berkeley for very valuable discussions. The inspiring atmosphere at these laboratories has been of the greatest importance during the course of this investigation.

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Tryckt den 2 november 1960

Uppsala 1960. Almqvist & Wiksells Boktryckeri AB